



Design considerations for low-temperature hydrocarbon oxidation reactions on Pd based catalysts

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ABSTRACT

Palladium-based catalysts are well known for their catalytic activity in hydrocarbon oxidation reactions in exhaust emission control. There is a need to develop catalysts that perform oxidation at low temperatures (< 300 °C), especially for future high efficiency combustion engines. In the present study, we investigate the role of Pd oxidation state in this temperature range for the oxidation of three different hydrocarbons (methane, propane and propylene). For each of these hydrocarbons, the reduced Pd catalyst was more active than the same catalyst after oxidation. Furthermore, when the reduced catalyst was tested under lean conditions, the activity for hydrocarbon oxidation declined due to formation of PdO. The addition of Pt helped to maintain Pd in a reduced state, even under lean conditions, and this is a major reason for improved performance of Pt-Pd catalysts compared to Pt or Pd alone. X-ray absorption near edge spectra (XANES) and temperature programmed reduction (TPR) experiments were used along with activity testing to understand the impact of the oxidation state of Pd on hydrocarbon oxidation performance. This study provides guidance in the development and operation of Pd catalysts for low temperature hydrocarbon oxidation.

1. Introduction

Among the platinum group metals, it is Pd that provides the highest catalytic activity for the complete oxidation of hydrocarbons in automotive exhausts (particularly for gasoline engine applications) and the combustion of methane in gas-powered turbines [1,2]. For diesel emissions after-treatment, palladium is commonly used in combination with platinum to catalyze oxidation reactions [3,4]. Together these two metals exhibit a synergistic relationship and are able to oxidize CO, hydrocarbons and NO produced by diesel engines while demonstrating remarkable hydrothermal stability not seen for Pt-only catalysts [3]. With the push towards higher efficiency engines, there is a need to achieve conversion of hydrocarbons at lower temperatures. Hence, this study focuses on the hydrocarbon oxidation performance of palladium catalysts which are known to be very active for this reaction. The nature of the most active sites is still a matter of debate and it has been suggested that the most active sites could be attributed to bulk PdO [5,6], metallic Pd [7], a surface Pd oxide on metallic Pd [8–10], a PdO-rich surface [11], or co-existence of Pd and PdO [12]. In this study we set

out to reexamine the roles and relative reactivity of metallic Pd and PdO since this will help in the design and operation of low temperature catalysts for emission control.

The contradictory assignments for active sites of Pd catalysts are due, in part, to the facile and reversible conversion between Pd metal and PdO and because observations are often made under very different experimental conditions, especially in the case of methane oxidation. It is useful to consider the performance of methane oxidation in three temperature regimes (regime I < 400 °C, regime II 400 °C–700 °C and regime III > 700 °C) [13]. These temperature regimes should be considered in the context of the temperature for PdO decomposition to form Pd metal, which is 877 °C in 1 atm of O₂ [14]. Above the decomposition temperature (which depends on the prevailing oxygen pressure), the only observed phase is Pd metal. However, at the high temperatures encountered in regime III the kinetics are so rapid that both phases are found to be active for methane oxidation [1,15,16]. Below the decomposition temperature, the thermodynamically stable phase is PdO. The phase rule predicts a single equilibrium temperature for two immiscible phases (Pd and PdO) hence one would expect the

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catalyst to exclusively contain PdO below the decomposition temperature and only Pd metal above this temperature. However, regime II is unique since it is possible to sustain co-existing Pd and PdO phases [15,17]. This is because Pd metal exposed to oxygen at high temperatures forms a strongly bound surface oxide that passivates the metal and prevents the formation of bulk oxide [15,18]. It was shown by Conrad et al. [18] that an unreactive surface oxide was formed on Pd when exposed to $\sim 700^\circ\text{C}$ at high oxygen pressures. McCarty [15] showed that the decomposition of this strongly bound oxide occurred at a temperature $> 900^\circ\text{C}$ while bulk PdO decomposed at 680°C in the flowing inert gas used in their experiments.

In the regime II, the rate of methane oxidation is found to increase with the degree of Pd oxidation to form PdO [1,15,16,19]. But the results observed in regime II should not be extrapolated to regime I because when Pd metal is studied at high temperatures it is passivated by the strongly bound oxygen, making it unreactive to methane oxidation and also to formation of bulk oxide. This is the reason that a catalyst containing co-existing Pd and PdO can continue indefinitely in regime II with invariant phase composition, unless perturbed. When this steady state is perturbed by lowering the temperature, there is an increase in the amount of PdO and a new steady state is established [16]. If this were to be an equilibrium state of the catalyst, then the relative amounts of Pd and PdO would be reversible, which is not the case in regime II. However, it was shown by Chin et al. [19] that the system can be made to approach thermodynamic equilibrium when methane and oxygen are both present, because of the redox nature of the reaction mixture. The resistance of Pd to oxidation during cooling, after heating beyond the PdO decomposition temperature, results in the well-known hysteresis in methane oxidation rates [1,15]. The co-existence of Pd and PdO represents a metastable state due to the presence of passivated Pd metal which resists oxidation [15,16]. Otherwise, especially in regime I, the oxidation of Pd to form PdO is quite facile [20]. Su et al. [20] reported that CH_4 decomposition does not readily occur on PdO, and reduction by methane involves an induction period where Pd nuclei form, after which it is rapid. These observations prompted us to examine the reactivity of metallic Pd in regime I, which is particularly relevant to developing catalysts for low temperature hydrocarbon oxidation.

As already mentioned, the complicating factor for determining the active state in regime I is the conversion of the Pd into the PdO under reaction conditions. Operando XANES was used by Nilsson et al. [12] to study the reactivity of Pd catalysts at 300°C , 400°C and 500°C while oxygen flow was pulsed on and off. As expected, switching off the O_2 caused the catalyst to transform from 100% PdO to 100% Pd metal, except at low temperatures where the kinetics of phase transformations were slow. Interestingly, the authors found that the highest reactivity for methane conversion was obtained in the regime where oxygen was switched off. They implied that the co-existence of metallic Pd and PdO may be necessary to achieve the highest reactivity at low temperatures. But there is no detailed characterization yet reported on the nature of the mixed Pd-PdO sites in a working catalyst. Our previous work [16] shows that Pd and PdO can co-exist, but as separate phases, in regime II. If PdO formed as a shell on the surface of Pd metal, we would not expect to see reactivity spanning that of metallic Pd and PdO. The picture is different in regime I since Pd exposed to oxygen can form a monolayer, and then bulk PdO [20], which is why the reactivity changes irreversibly as the catalyst is exposed to oxidizing conditions, from that of Pd metal to that of PdO, as we show in this work.

A recent study of methane oxidation on $\text{Pd}/\text{Al}_2\text{O}_3$ by in-situ DRIFTS concluded that low temperature activity could indeed be associated with the metallic state of Pd [21]. A DFT calculation of methane oxidation also comes to the conclusion that the barrier for methane oxidation on metallic Pd (especially small particles) is lower than that on bulk PdO [22]. In regime I, we can rely on the sluggish kinetics of Pd oxidation [20] that provide a window where the catalyst is initially in the form of a metal (perhaps covered with a monolayer of oxygen) and

then gradually transforms into PdO. In this work, we follow industry-standard light off protocols to systematically compare the performance of pre-reduced Pd and fully oxidized PdO in hydrocarbon oxidations (methane, propane and propylene). We also used in-situ X-ray absorption near edge spectroscopy (XANES), and temperature programmed reduction (TPR) measurements to correlate the reactivity with catalyst structure. The comparison of reactivity of metallic Pd and PdO provides insight into the factors responsible for low temperature hydrocarbon oxidation activity.

2. Experimental

2.1. Catalyst preparation

Both washcoated monolith catalysts in a tubular reactor and powder catalysts in a packed bed microreactor were evaluated. The catalyst support used in all studies is a powder La-alumina catalyst support (MI-386) containing $\sim 4\text{ wt.}\%$ La_2O_3 , with a BET surface area of $176\text{ m}^2\text{g}^{-1}$. The La-alumina support was denoted as Al_2O_3 in this work.

For methane oxidation, a powder $\text{Pd}/\text{Al}_2\text{O}_3$ (2 wt.% Pd) and a Pt-Pd/ Al_2O_3 (4 wt.%Pt and 2 wt.% Pd) was prepared by incipient wetness by using an aqueous solution of a 10 wt.% palladium(II) nitrate solution in 10 wt.% nitric acid. The $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst was then calcined in air at 800°C for 10 h. The powder Pt-Pd/ Al_2O_3 catalyst was prepared by impregnating chloroplatinic acid precursor (4 wt.% Pt) on the obtained $\text{Pd}/\text{Al}_2\text{O}_3$ powder catalyst (2 wt.%Pd, pre-calcined at 800°C) and drying at 120°C for 10 h, followed by calcining at 650°C for 10 h in flowing air to form PtPd alloy.

For propane oxidation, a 1.1 wt% $\text{Pd}/\text{Al}_2\text{O}_3$ powder catalyst was prepared using the incipient wetness. $\text{Pd}(\text{NO}_3)_2$ precursor was introduced to lanthanum-stabilized alumina support (MI386) after having been diluted with DI water. The slurry was dried at 120°C overnight and calcined at 550°C for 2 h in ambient air. The weight loading after calcination was confirmed via inductively coupled plasma spectroscopy (ICP) performed by Galbraith Laboratories Inc.

For propylene activity tests, two different Pd catalysts were used. For experiments evaluating the impact of various oxidation/reduction pretreatments (Figs. 1–3) a model washcoated cordierite monolith catalyst with $50\text{ g}/\text{ft}^3$ $\text{Pd}/\text{Al}_2\text{O}_3$ from a catalyst manufacturer was used. This catalyst was degreened at 750°C for 2.4 h in a flow of 10% $\text{H}_2\text{O}/\text{air}$ prior to activity testing. For tests of fresh and mildly aged $\text{Pd}/\text{Al}_2\text{O}_3$, Pt/ Al_2O_3 and Pt-Pd/ Al_2O_3 (Fig. 5) catalysts, Al_2O_3 -supported Pt and Pd powders were synthesized using the conventional wet impregnation method. Precursor solutions of chloroplatinic acid and palladium

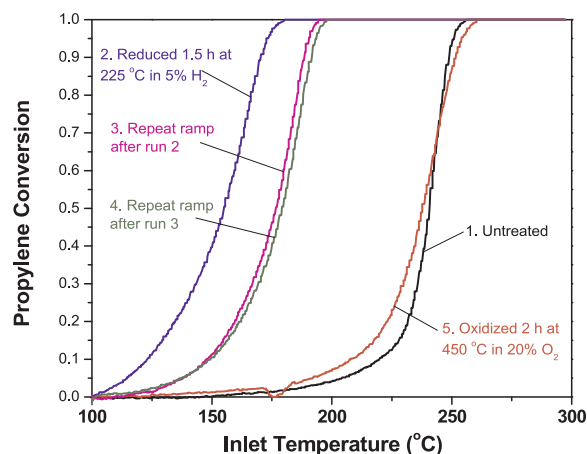


Fig. 1. Propylene light-off curves as temperature was raised from 100 to 300°C in reaction conditions described in Table 1 (row F) for model $\text{Pd}/\text{Al}_2\text{O}_3$ ($50\text{ g}/\text{ft}^3$) catalyst after various treatments; oxidation feed conditions described in Table 1 (row A); reduction feed conditions described in the Table 1 (row C).

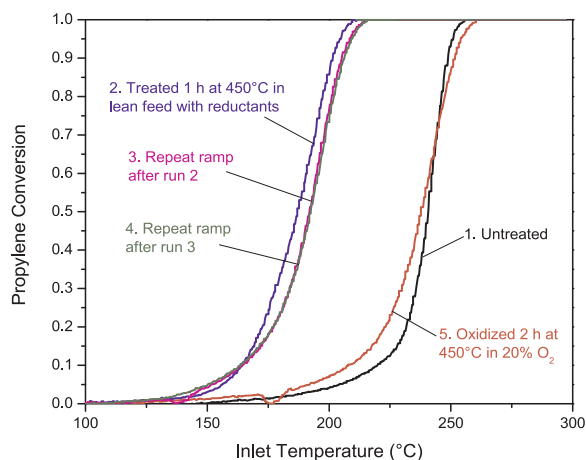


Fig. 2. Propylene light-off curves as temperature was raised from 100 to 300 °C in reaction feed described in Table 1 (row F) for model Pd/Al₂O₃ (50 g/ft³) catalyst after various treatments; oxidation feed conditions described in Table 1 (row A); reduction feed conditions described in Table 1 (row E).

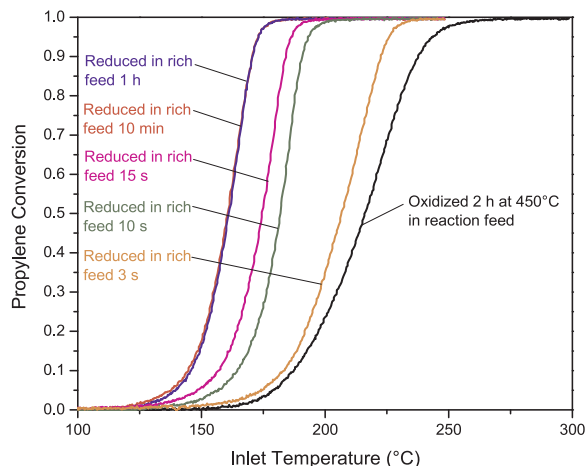


Fig. 3. Propylene light-off curves as temperature was raised from 100 to 300 °C in reaction feed described in Table 1 (row G) for model Pd/Al₂O₃ (50 g/ft³) catalyst after various treatments at 225 °C; Note: oxidation was performed prior to each reduction treatment; oxidation feed conditions described in Table 1 (row B); reduction feed conditions described in Table 1 (row D).

nitrate (both prepared in-house) were diluted with deionized water and introduced to MI-386 and mixed vigorously to form thin slurries. The slurries were individually dried then calcined for 1 h at 500 °C in air. Two powders were prepared, 1.451 wt% Pt and 1.451 wt% Pd. The bimetallic samples were made by physically mixing the two powders. For reactivity experiments the resulting slurries were then washcoated onto 400/4 cordierite substrates to a loading of 120 g/L resulting in 50 g/ft³ total metals loading. After washcoating, the remaining slurries were dried and crushed for use in TPR and XANES experiments.

2.2. Catalyst characterization

X-ray absorption spectroscopy (XAS) experiments were conducted at beamline 10-ID-B of the Advanced Photon Source at Argonne National Laboratory. Measurements of fresh and aged catalysts were taken at room temperature at the Pd K edge and Pt L3 edge. Each powder catalyst sample was ground to a fine, uniform consistency before being loaded into a sample holder. The sample holder consisted of a stainless steel die in which powder sample was pressed to form a self-supporting plug. The die was then loaded into a sample cell consisting of a 3/4 in. ID quartz tube with X-ray transparent endcaps and fittings

for flowing gases through the quartz tube; this sample cell was mounted on a movable sample stage to align the sample in the beam path. The amount of catalyst loaded was selected to obtain an edge step of approximately 0.3–1.0 for the chosen experiment, and varied from 20 to 70 mg. A gas delivery system using mass flow controllers was used to mix and deliver gases (NO, O₂, N₂) at 50 cm³ min^{−1} total flow rate. In a typical experiment, the as-received catalyst was measured initially at 25 °C in 20% O₂ with N₂ balance, and then heated to 300 °C under 200 ppm NO and 3% O₂ with N₂ balance at a rate of approximately 25 °C min^{−1}. XAFS measurements were taken continuously at a rate of approximately once every 2.5 min. After 60 min, the sample was briefly purged with N₂ and 3.5% H₂ in N₂ was introduced to reduce the sample for 30 min, and the sample was again purged. The 200 ppm NO and 3% O₂ mixture was again introduced and XAFS were taken for an additional 60 min. Analysis of the near-edge portion of the spectra (x-ray absorption near edge spectroscopy; XANES) was utilized to determine the oxidation state of each metal to a high degree of accuracy by use of linear combination fitting (LCF) to metallic (Pt, Pd metal reference) and oxide (PtO₂ and PdO) standards.

Temperature programmed reduction (TPR) experiments were performed on a Micromeritics Autochem. II 2920. First, the catalysts were oxidized at 500 °C in 10% O₂ for 2 h. Then, TPR was performed under 10% H₂/Ar as the temperature was raised from −50 °C to 500 °C at a rate of 10 °C/min. After the sample was completely reduced, it was cooled back down to 50 °C in He. The reduction profiles were measured via both thermal conductivity detector within the instrument and a Pfeiffer OmniStar mass spectrometer.

2.3. Hydrocarbon oxidation experiments

2.3.1. Methane oxidation

Methane oxidation was performed in a packed bed quartz tube reactor. Catalyst powder samples of 20 mg were placed in the middle of the reactor. Gas flow rates were controlled by mass flow controllers. Reaction products were analyzed by an online micro-GC (Agilent 490). The gas mixture contained 2% CH₄, 5% O₂ and He as balance. Light-off measurements were carried out by heating the sample at a rate of 2 K min^{−1} from 100 to 900 °C. At 900 °C the PdO catalyst has transformed into metallic Pd. Next, the catalyst was cooled to study the re-oxidation of Pd metal that occurs during cool down, while methane oxidation reactivity was monitored.

2.3.2. Propylene oxidation

Propylene oxidation activities of the washcoated monolith samples were measured in a quartz tubular reactor at atmospheric pressure. The standard reaction feed stream consisted of 260 ppm C₃H₆, 90 ppm C₃H₈, 200 ppm NO, 8% O₂, and 8% H₂O, with balance N₂ as described in Table 1. The inlet gas temperature, measured approximately 2 mm from

Table 1

Feed compositions used for oxidation/reduction pretreatments and propylene light-off experiments.

	H ₂	CO	C ₃ H ₆	C ₃ H ₈	NO	O ₂	CO ₂	H ₂ O
(ppm unless specified as %)								
Oxidation Pretreatment								
A - Oxidation	–	–	–	–	–	20%	–	–
B - Reaction Feed Oxidation	–	500	260	90	200	8%	–	5%
Reduction Pretreatment								
C - Hydrogen Reduction	5%	–	–	–	–	–	–	–
D - Rich	0.5%	1.5%	370	130	200	0.5%	10%	10%
E - Slightly Lean	–	–	260	90	200	1%	8%	5%
Reaction Feed								
F - Standard	–	–	260	90	200	8%	–	5%
G - Standard plus CO	–	500	260	90	200	10%	8%	5%

the catalyst, was ramped from 100 to 300 °C at a rate of 2 °C/min while measuring the product stream concentrations with a Nicolet Nexus 670 Fourier Transform Infrared (FTIR) analyzer with a heated transmission cell for gas-phase analysis calibrated at 940 Torr and 165 °C. A pressure controller at the outlet of the FTIR was used to maintain calibration pressure in the gas cell. Catalyst aging was done in a box furnace with 10% H₂O and flowing air. Oxidation and reduction treatments in the reactor were performed by varying O₂, H₂, hydrocarbon and CO concentrations in the gas feed to achieve lean, slightly lean or rich conditions (see Table 1). For some tests a more representative feed containing 500 ppm CO, 260 ppm C₃H₆, 90 ppm C₃H₈, 10% O₂, 200 ppm NO, 10% H₂O, 10% CO₂ with balance N₂ was used since CO and CO₂ are commonly present in diesel exhaust. After oxidation treatments or reaction measurement experiments the feed composition was maintained during cooling. After reduction treatments samples were cooled in N₂. All monolith reactor tests were performed on samples cut to 0.75 in. diameter by 0.45 in. length at a flow rate of 1.6 L/min resulting in a gas hourly space velocity of 30,000 h⁻¹.

2.3.3. Propane oxidation

Propane oxidation was carried out in quartz tube reactor on 1.1 wt.% Pd/Al₂O₃ catalyst. The reactor contained 25 mg of 1.1 wt.% Pd/Al₂O₃ mixed with 25 mg SiO₂ diluent. All experiments involved pre-oxidation of the sample first in 5% O₂ at 500 °C for 1 h in order to burn off any coke that may have deposited during previous experiments. After pretreatment in oxygen, the reduced sample was obtained by reducing in 5% H₂ at 250 °C for 0.5 h. The catalyst was then cooled to 100 °C in 5% H₂ in order to ensure Pd remained metallic before reactivity measurements. Pre-oxidizing experiments involved heating the catalysts in 5% O₂ at 500 °C for 1 h. The reaction feed contained 0.05% C₃H₈, 5% O₂ and 5% H₂O with a total flow rate of 0.32 L/min (nitrogen carrier gas).

3. Results and discussion

3.1. Monometallic Pd catalyst for hydrocarbon oxidation

The propylene oxidation activity of the degreened 50 g/ft³ Pd/Al₂O₃ model monolith catalyst was tested after reduction in 5% H₂ for 1.5 h at 225 °C, and after oxidation with 20% O₂ for 2 h at 450 °C. The results are shown in Fig. 1. Without pretreatment (1. Untreated), the catalyst light-off temperature (temperature of 50% conversion) is ~ 240 °C, but after H₂ reduction, the light-off shifts to 155 °C, nearly 100 °C lower, indicating that the reduced Pd/Al₂O₃ is significantly more active for propylene oxidation than the untreated catalyst. After the H₂ treatment, the Pd is primarily in the metallic Pd⁰ state indicating that Pd⁰ is more active than PdO for propylene oxidation in a lean feed. The activity decreases slightly for the second consecutive run after reduction and the light-off temperature shifts to higher temperature by ~ 25 °C, indicating that the reduced Pd is partially oxidized during the first propylene oxidation experiment as the temperature is raised to 300 °C in the reaction feed containing 8% O₂. The light-off temperature increases very slightly for the next consecutive ramp experiment (run 4 in Fig. 1), due to the slow kinetics of PdO formation at this temperature. Thus the catalyst appears to have reached a stable mixture of Pd oxide/metal for the given reaction conditions. However, after the catalyst is re-oxidized at 450 °C (run 5 in Fig. 1), its catalytic behavior returns to the poor performance of the untreated catalyst.

The oxidation state of Pd can change under reaction conditions, which impacts its performance significantly. Fig. 2 shows propylene light-off of the Pd model catalyst but after a “reduction” treatment performed in a mixture similar to the reaction feed but with O₂ concentration of only 1% rather than 8% (as described in Table 1, row E). When treated at 225 °C for 1.5 h in this slightly lean feed including reductants, the light-off temperature is ~ 50 °C lower than when treated in 20% O₂ (see Fig. 2). The state of Pd is therefore easily changed and the Pd exists as a mixture of Pd⁰ and PdO. Even under

these lean conditions, Pd is partially reduced, most likely due to the fact that propylene adsorbs more strongly than oxygen on Pd, however the extent of the reduction is less than observed in Fig. 1 where the sample was reduced in 5% H₂. Runs 3 and 4 in Fig. 2 were run consecutively after run 2 without additional pretreatment and exhibit very similar light-off activity to run 2, indicating that the further oxidation of Pd is very slow during exposure to reaction conditions up to 300 °C.

In addition to feed composition and temperature, reductant exposure duration is also critical to the state of Pd in a Pd/Al₂O₃ catalyst. The same model Pd/Al₂O₃ catalyst was exposed to the rich feed described in Table 1 (row D) for various lengths of time. Before each rich exposure, the catalyst was oxidized at 450 °C for 2 h in the reaction feed containing CO (Table 1, row G). The baseline activity in the same reaction feed after oxidation is shown in Fig. 3 (black curve). After treatment at 225 °C for 1 h in the rich feed the propylene light-off temperature is similar to that observed after reduction in Fig. 1 where 5% H₂ was used as the reductant indicating that the Pd is metallic (see Fig. 3). In fact, 10 min reduction in this rich feed is still as effective as 5% H₂ in reducing Pd to metal based on the performance in Fig. 3. However, as the reduction duration decreases to the order of seconds, the extent of reduction is diminished and the catalyst does not reach a fully-reduced state after rich pretreatment. This indicates that the PdO to Pd metal transformation process is kinetically controlled under these experimental conditions.

In view of the considerable debate as to the identity of the active state of Pd for various hydrocarbon oxidation reactions, it is of interest to consider whether these findings would apply to other hydrocarbon species. Two other hydrocarbons that are common in automotive exhaust and have been widely studied are propane and methane. These hydrocarbons are more difficult to oxidize than propylene and are thought to behave differently than alkenes on Pd catalysts. Therefore, we investigated the reactivity of a Pd/Al₂O₃ catalyst (2 wt.% Pd) for methane and propane oxidation before and after H₂ reduction (7% H₂/Ar). The methane oxidation light-off curves of the Pd/Al₂O₃ catalyst before and after H₂ reduction are shown in Fig. 4a. The Pd/Al₂O₃ catalyst shows an onset of reactivity at ~ 280 °C and methane conversion reaches 100% at ~ 480 °C. After reduction in H₂ at 200 °C, the reduced Pd/Al₂O₃ catalyst was tested for methane oxidation from room temperature to 600 °C. The results show that the light-off temperature of the methane oxidation shifts to lower temperatures compared to the calcined Pd/Al₂O₃ catalyst (Fig. 4a). The temperature was lowered to room temperature in the flowing CH₄/O₂ and the catalyst tested again from room temperature to 600 °C. It can be seen that the light-off curve for the second run of the reduced Pd/Al₂O₃ catalyst is similar to that of the calcined Pd/Al₂O₃ catalyst. These results indicate that the reduced Pd/Al₂O₃ catalyst is more active than the oxidized Pd/Al₂O₃ catalyst for methane oxidation. It is also evident that the metallic Pd on the reduced Pd/Al₂O₃ becomes completely oxidized during methane oxidation (100–600 °C), which caused the second run to exhibit similar catalytic behavior as the pre-oxidized Pd/Al₂O₃ catalyst for methane oxidation.

The propane oxidation light-off curves of the Pd/Al₂O₃ catalyst (1.1 wt.% Pd) before and after 5% H₂/Ar reduction are shown in Fig. 4b. The initial oxidation state of Pd was controlled by pretreating the catalyst under reducing/oxidizing conditions. All experiments involved pre-oxidation of the sample first in 5% O₂ at 500 °C for 1 h in order to burn off any coke that may have deposited during previous experiments. After pretreatment in oxygen, the reduced sample was obtained by reducing in 5% H₂ at 250 °C for 0.5 h. The catalyst was then cooled to 100 °C in 5% H₂ in order to ensure Pd remained metallic before reactivity measurements. Pre-oxidizing experiments involved heating the catalysts in 5% O₂ at 500 °C for 1 h. The catalyst was cooled to 100 °C in 5% O₂ in order to ensure PdO_x did not get reduced to Pd⁰ prior to the reactivity measurements. Fig. 4b shows the temperature-programmed propane oxidation measurements after the pretreatments. It is clear that pre-reducing the catalyst improved the performance compared to pre-oxidation. These results indicate that reactivity for

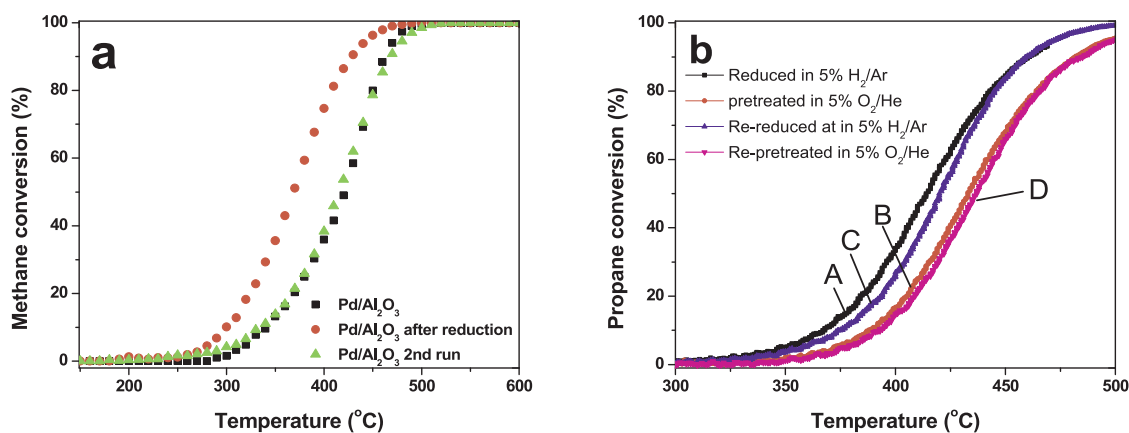


Fig. 4. (a) Methane oxidation conversion as a function of temperature over a Pd/Al₂O₃ catalyst (2 wt.%Pd) after different treatments. The gas mixture contained 2% CH₄, 5% O₂ and He as balance. (b) Propane oxidation conversion as a function of temperature over Pd catalysts (1.1 wt.%Pd) after different pretreatments. (A) Pd/Al₂O₃ catalyst was pretreated at 250 °C for 0.5 h in a flow of 5% H₂/Ar. (B) the reduced Pd catalyst from (A) was pretreated at 500 °C for 1 h in 5% O₂/He. (C) the catalyst (B) was pretreated at 250 °C for 0.5 h in a flow of 5% H₂/Ar. (D) the reduced Pd catalyst from (C) was pretreated at 500 °C for 1 h in 5% O₂/He. Reaction feed: 0.05% C₃H₈/5% O₂/5% H₂O, Ramp Rate = 2 °C/min.

propane oxidation is enhanced when the initial oxidation state of Pd is Pd⁰.

The above light-off curves show that the reduced Pd/Al₂O₃ catalyst is more active than the calcined Pd/Al₂O₃ catalyst in hydrocarbon oxidations. In order to verify that the reduced Pd catalyst is more active than oxidized Pd catalyst in hydrocarbon oxidation under steady state, we further compared the steady-state reactivity of Pd/Al₂O₃ catalysts before and after H₂ reduction when the reaction temperature in methane oxidation was kept at 350 °C (Figures S2 and 3). As can be seen, the steady-state reactivity in methane oxidation also indicated that the reduced Pd/Al₂O₃ catalyst is more active than the calcined Pd/Al₂O₃ catalyst at 305–350 °C. We further explored the morphologies of the Pd/Al₂O₃ catalysts using HRTEM before H₂ reduction, after H₂ treatment and after methane oxidation. The calcined Pd/Al₂O₃ catalyst shows the irregular shape of the PdO phase, displayed in Fig. 5 and Figure S1. The HRTEM image of Pd/Al₂O₃ after reduction in H₂ shows that the phase is metallic Pd (Fig. 5b). From Fig. 5c, we observed the presence of metal Pd, indicating that the Pd metal persists after methane oxidation at 350 °C for 30 min (Fig.S3).

3.2. Bimetallic Pt-Pd catalyst for low-temperature hydrocarbon oxidation

The poor performance for hydrocarbon oxidation of oxidized Pd/Al₂O₃ has been demonstrated under lean conditions. For this reason Pd is typically combined with Pt in commercial diesel oxidation catalysts (DOC) in order to improve performance³. Fig. 6 shows three fresh catalysts (Pd/Al₂O₃, Pt/Al₂O₃, and PtPd/Al₂O₃), all with poor activity for propylene oxidation and exhibiting light-off temperatures above 240 °C. After mild aging of the PtPd/Al₂O₃ catalyst for 2 h at 300 °C with 10% O₂ and 10% H₂O the light-off temperature decreases by ~70 °C to 170 °C. For either monometallic catalyst the same mild aging

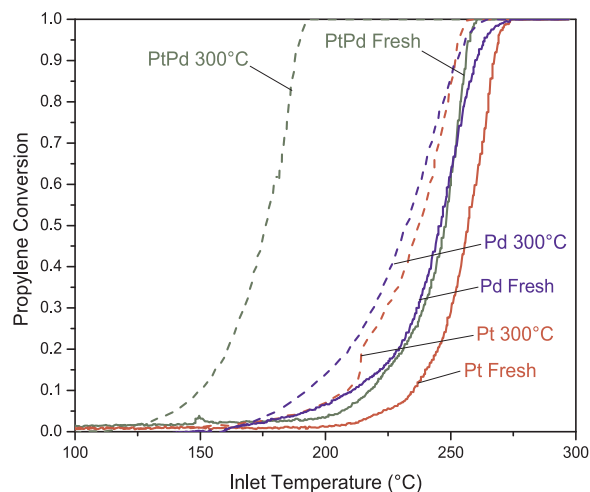


Fig. 6. Propylene oxidation conversion as a function of temperature for fresh and mildly aged Pd/Al₂O₃, Pt/Al₂O₃ and PtPd/Al₂O₃ catalysts (mild aging conditions: 2 h/ 300 °C/ 10% O₂/ 10% H₂O balance N₂); reaction conditions described in Table 1 (row F).

at 300 °C has little impact on propylene oxidation performance. The improvement observed by combining and aging the PtPd/Al₂O₃ catalyst is similar to that observed in Figs. 1–3 when Pd/Al₂O₃ was reduced prior to propylene light-off experiments. The effect of adding Pt to a Pd/Al₂O₃ catalyst appears to have a similar impact on the performance of Pd as that of a reduction treatment.

The low temperature activity of the reduced Pd and PtPd catalysts was also investigated as a function of time on stream for methane

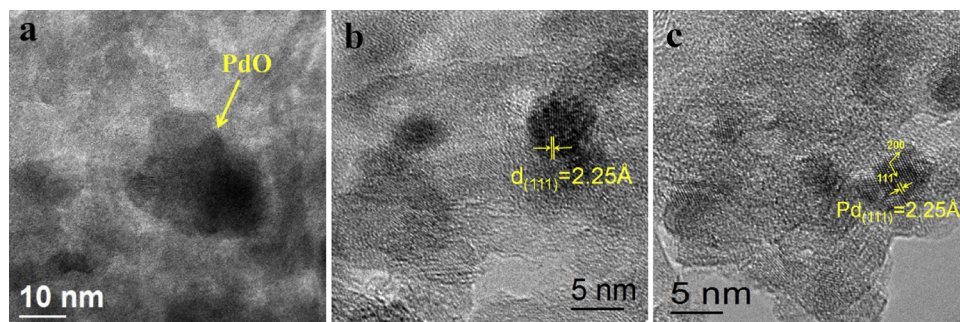


Fig. 5. TEM images of Pd/Al₂O₃ catalyst after different pretreatments, (a) oxidized Pd/Al₂O₃ calcined at 800 °C for 10 h; (b) reduced Pd/Al₂O₃ in H₂ at 250 °C showing the lattice fringes of metallic Pd, indicating the presence of metallic Pd; (c) the reduced Pd/Al₂O₃ after performing methane oxidation at 350 °C for 30 min (steady-state reactivity data is shown in Figure S3).

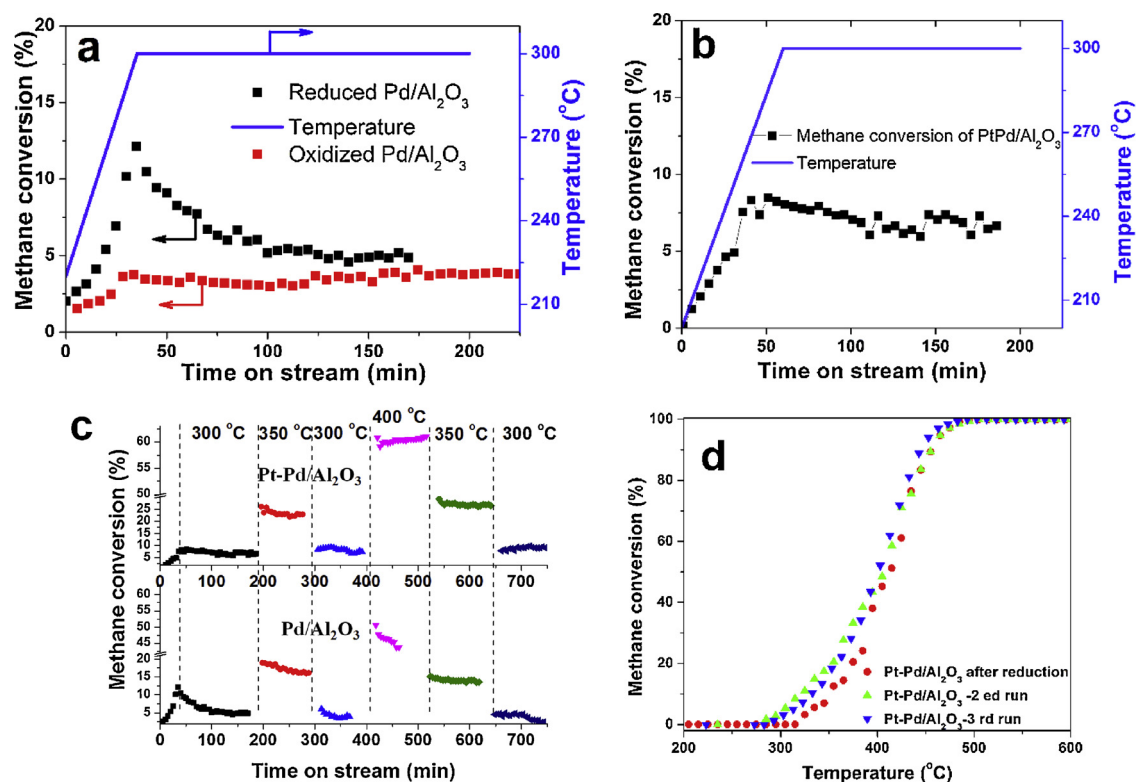


Fig. 7. Methane oxidation conversion as a function of (a–c) time and (d) temperature over (a) Pd/Al₂O₃, (b) Pt-Pd/Al₂O₃ and (c) Pd/Al₂O₃ and PtPd/Al₂O₃ catalysts after reduction at 250 °C for 2 h in a flow of H₂; (d) light-off curves of PtPd/Al₂O₃ catalyst in methane oxidation.

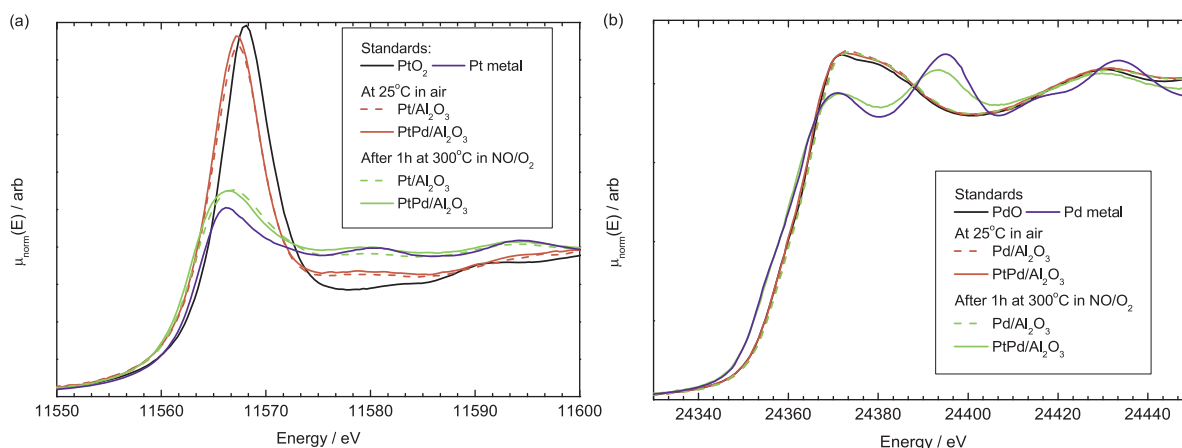


Fig. 8. XANES at the Pt L3 edge (a) and Pd K edge (b) of catalysts, along with oxide and metal standards; Measurements taken at 25 °C (as received) and after exposure to 200 ppm NO, 3% O₂ and balance N₂ at 300 °C for 60 min.

oxidation (Fig. 7). As shown in Fig. 6a, the reduced Pd/Al₂O₃ catalyst shows a rapid deactivation when the reaction temperature is kept at 300 °C after increasing from room temperature to 300 °C. After ~1 h time on stream at 300 °C, the pre-reduced Pd/Al₂O₃ catalyst approaches the reactivity of the initial Pd/Al₂O₃ catalyst, i.e. oxidized catalyst (Fig. 7a). This suggests that the metallic Pd on pre-reduced Pd/Al₂O₃ catalyst gets reoxidized to PdO with time on stream at 300 °C, showing similar catalytic behavior as the initial catalyst. However, the PtPd/Al₂O₃ catalyst shows much more stable methane conversion when the temperature reaches 300 °C after the reduction in H₂ (Fig. 7b). Since the PtPd catalyst does not undergo oxidation (as will be shown later), the reactivity of PtPd/Al₂O₃ is higher than the pre-reduced Pd/Al₂O₃ catalyst at 300 °C at steady state (i.e. after 2 h).

The reactivity of the pre-reduced Pd/Al₂O₃ and PtPd/Al₂O₃ catalysts was also tested when the reaction temperature was increased step-

wise from 300 to 400 °C. When the reaction temperature was increased to 350 °C and further to 400 °C, the reactivity was found to increase with the reaction temperature (Fig. 7c). After the temperature was cooled down to 300 °C, the reactivity approached that of the initial Pd/Al₂O₃ catalyst (i.e. oxidized catalyst). However, for the PtPd/Al₂O₃ catalyst aged at 650 °C (Fig. 7b), no decrease in the methane conversion was observed when the reaction temperature was brought back to 300 °C and maintained at 300 °C. This means that the Pd on the PtPd/Al₂O₃ catalyst does not get oxidized during the reaction at low temperature. This is also evident in the light-off experiments for the PtPd/Al₂O₃ catalyst as shown in Fig. 7d. The second and third runs for the PtPd/Al₂O₃ catalyst show similar light-off curves as the first run when the reaction temperature increases from room temperature to 600 °C, indicating that PtPd does not undergo changes in oxidation state.

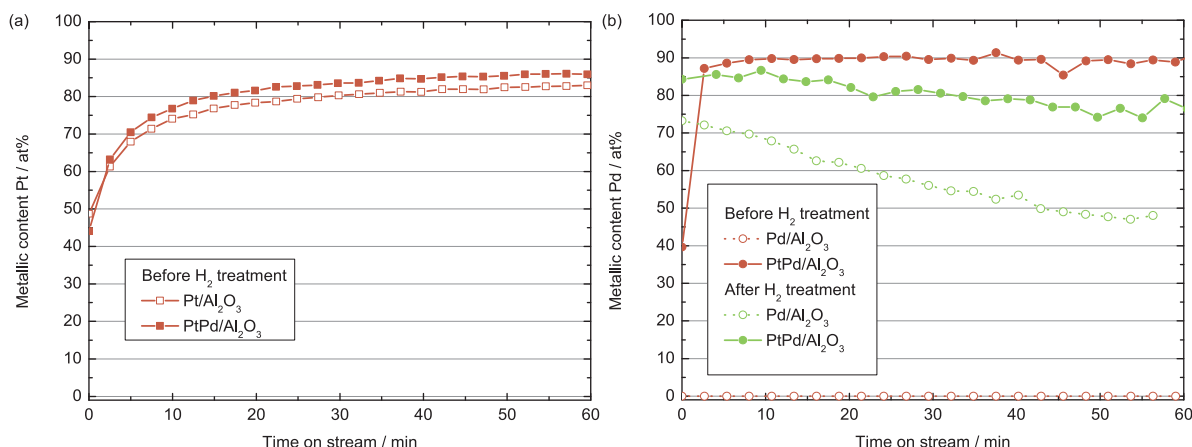


Fig. 9. (a) Metallic Pt content and (b) metallic Pd content for Pt, Pd and PtPd samples at 300 °C with 200 ppm NO, 3% O₂ and N₂ as balance gas; the compositions were measured for 1 h in situ starting from fresh state (before H₂ treatment) or after H₂ treatment.

3.3. In-situ catalyst characterization

X-ray absorption near edge spectra (XANES) provide insights into the changes in the state of the metals in Pd, Pt and PtPd/Al₂O₃ catalysts. As shown in Fig. 8a, prior to exposure to reaction conditions, the Pt in both Pt and PtPd catalysts was in an oxidized state similar to PtO₂. But after 1 h at 300 °C under reaction conditions (200 ppm NO and 3% O₂), the Pt in both catalysts was almost completely reduced to Pt metal. Pd was also in an oxidized state in both fresh catalysts (Fig. 8b), but unlike Pt, the Pd-only catalyst remained oxidized after 1 h under reaction conditions. When combined with Pt, however, the Pd was reduced to metal under reaction conditions. Hence Pt appears to facilitate the reduction of PdO, whereas Pt is reducible irrespective of the presence of Pd.

In-situ XANES spectra were collected for 1 h under an NO/O₂ feed to examine the time-resolved changes in the states of Pt and Pd. Fig. 9 shows the metallic content of Pt and Pd in the different samples under an NO/O₂ feed. Starting from fresh samples, Pt in both monometallic and bimetallic catalysts was quickly reduced to metal under reaction conditions, gradually approaching an equilibrium oxidation state of approximately 85% metallic Pt (Fig. 9a). However, while the Pd in the monometallic catalyst remained completely oxidized, Pd in PtPd catalyst was reduced to 90% metallic in 5 min (Fig. 9b).

When exposed to the NO/O₂ feed, after an H₂ treatment, Pd was oxidized at a constant rate (0.49% min⁻¹) during reaction, while Pt (not shown) remained 85% metallic. For the bimetallic catalysts, Pd in PtPd oxidized at a slower rate (0.18% min⁻¹). The slow re-oxidation of Pd in the PtPd catalysts may be attributed to Pt-Pd surface being resistant to oxidation while the Pd particles which have not alloyed with Pt continuing to oxidize. In previous work we have reported such a phase segregation of Pt-Pd catalysts [23]. These results show that Pt not only facilitates the reduction of PdO [24] but also helps to keep Pd in a metallic state under oxidizing conditions [25]. As Pd metal is more active for hydrocarbon oxidation, the ability of Pt to facilitate the reduction of Pd and stabilize Pd⁰ may explain the improved activity and stability of the bimetallic catalyst for propylene and methane reactions shown in Figs. 6 and 7.

The ability of Pt to help stabilize Pd in a metallic state is also supported by TPR experiment. As shown in Fig. 10, for the fresh Pd/Al₂O₃ catalyst, there is a large reduction peak at 16 °C due to the reduction of the PdO formed during oxidation of this catalyst at 500 °C with 10% O₂. Aging the Pd catalyst decreases the size of the reduction peak but not the reduction temperature, which is likely due to particle growth. Further evidence for particle growth comes from the presence of a hydride decomposition peak which is only seen in the aged catalysts (arrow, Fig. 10).

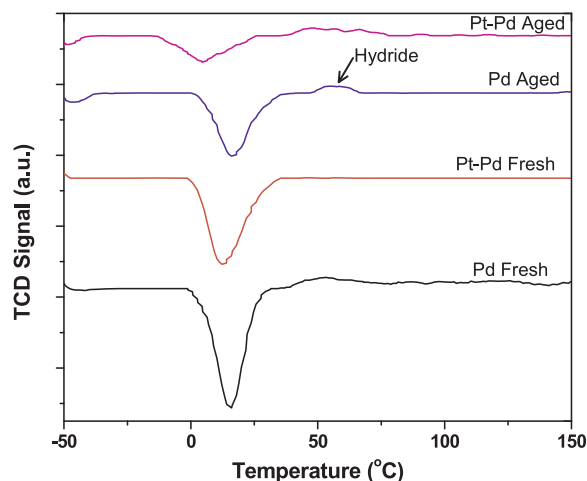


Fig. 10. TPR patterns of Pd and PtPd catalysts; Aged samples treated in air for 2 h/750 °C/10% H₂O.

When combined with Pt, the reduction peak shifts to a somewhat lower temperature as Pt helps to facilitate the reduction of Pd. It is important to note that the catalysts labelled “fresh” have in fact been pretreated at 500 °C in 10% O₂ for 2 h allowing the Pt and Pd to alloy to some extent. The ability of Pt to keep Pd metallic is even more clearly observed on the aged PtPd/Al₂O₃ catalyst. After aging at 750 °C for 2 h, the catalyst has been alloyed to a greater extent and there is very little reduction observed.

3.4. Discussion

A recent study concludes that the PdO is the “most active phase” for methane oxidation [6]. However, since the catalysts were always subject to oxidation prior to reaction, there was no direct comparison between reduced and oxidized Pd catalysts [6]. The goal of the present study was to examine the activity of Pd-based catalysts for hydrocarbon oxidation to determine if the metal or the oxide phase is more active in the low temperature range ($T < 400$ °C) which is regime I for the oxidation of methane as described in the introduction. In this temperature range, when a metallic Pd catalyst is heated in air, or under lean reaction conditions, oxygen chemisorbs on the surface [20] and at higher temperatures (~ 300 °C or above) the formation of the bulk oxide PdO starts to occur. This is seen clearly in our in-situ measurements via XANES (Fig. 9) and via TPR (Fig. 10). When Pt is present along with Pd, the formation of the bulk oxide is prevented, and the catalyst remains in metallic form. This is seen clearly via in-situ

measurements via x-ray absorption spectroscopy in this work (Fig. 10) and has also been observed in previous studies of Pt-Pd catalysts [23]. HRTEM measurements show metallic surfaces with no evidence of a surface oxide (chemisorbed oxygen cannot be imaged with this technique) unless the Pd concentration reaches the limit of stability where Pd will phase segregate to form bulk PdO. A recent study of Pt emission from Pt-Pd bimetallic particles showed that this limit of stability corresponds to an atomic concentration of ~ 70 atom% Pd. When this concentration is reached, the excess PdO starts to form as a separate phase [26]. Since the catalysts used in this study had lower concentrations of Pd in each particle, no surface PdO phase is expected to occur on the surface of the Pt-Pd catalysts. Hence, these catalysts provide the best opportunity to examine the role of reduced Pd metal for hydrocarbon oxidation. The results presented here show that the reduced catalyst containing metallic Pd is more active than the pre-oxidized catalyst. However, the higher reactivity of the metallic Pd is lost after the first experiment under oxidizing conditions due to progressive formation of the PdO phase (Fig. 1–3). The rate of Pd oxidation is more rapid at higher temperatures, hence we see that the difference in reactivity between the metallic and oxide form of Pd is most pronounced for propylene oxidation (T_{50} for Pd metal is ~ 100 °C lower than for PdO) which takes place at temperatures below 250 °C, while for propane or methane oxidation the difference in T_{50} between a reduced and oxidized catalysts is less than 50 °C.

The performance improvement achieved by combining Pt with Pd and treating at elevated temperatures (≥ 300 °C) in O_2 -containing gaseous mixtures was comparable to that obtained by reducing the Pd-only catalyst. The difference in reactivity between reduced Pd and the Pt-Pd catalyst is very small, both for methane and propylene oxidation. Hence we cannot attribute this activity enhancement to the promotion of Pd by Pt nor the reactivity of Pt itself. A recent study of methane oxidation also found an enhancement in methane oxidation activity when Pt-Pd was compared with a Pd only catalyst [22]. However, the authors did not comment on the phase of the Pd. It is likely that the Pd-only catalyst was in an oxidized state, in which case the performance improvement they reported is very similar to that seen in this work, since it corresponds then to the difference between reduced and oxidized Pd. We attribute the effect of Pt on Pd to the ability of Pt to reduce PdO and form metallic Pt-Pd even under oxidizing conditions. On both model and powder PtPd catalysts [17,24], Pt species were found to migrate readily due to the high vapor pressure of PtO_2 and become trapped by PdO to form PtPd particles. Our XANES and TPR results clearly show how Pd stays in a metallic state in the PtPd/ Al_2O_3 catalysts at temperatures ≥ 300 °C in a feed containing O_2 . In these hydrocarbon oxidation reactions, Pt is less active than Pd. Our results suggest that the ability of Pt to keep Pd metallic is a major contributor to the improved performance of PtPd catalysts compared to Pd alone for lean hydrocarbon oxidation reactions. However, maintaining a high dispersion of the Pt-Pd remains a challenge since the sintering of the metallic Pt-Pd in oxidizing conditions via Ostwald ripening is quite rapid at 650 °C [25]. This is because while Pd helps to slow the sintering of Pt by lowering its vapor pressure (through alloy formation) and trapping mobile PtO_2 , the presence of Pt tends to increase the rate of sintering of Pd which is seen through the presence of larger crystallites of PdO in Pt-Pd catalysts containing excess Pd, compared to Pd-only catalysts heated in air at 800 °C [26]. These considerations will provide guidance in future design of thermally durable low temperature hydrocarbon oxidation catalysts.

4. Conclusions

The low-temperature catalytic performance of Pd/ Al_2O_3 and PtPd/ Al_2O_3 catalysts in three hydrocarbon oxidation reactions (methane, propane and propylene) was studied. The most reactive hydrocarbon, propylene, allows us to perform oxidation at a low temperature so that Pd can be retained in metallic form. On the other hand, during methane

oxidation, the catalyst gradually transformed into PdO. A range of catalyst preparations and morphologies (monoliths or powders) were used and the results were consistent with reduced Pd catalyst always being more active than the oxidized Pd catalyst in feeds containing excess O_2 . The Pd/ Al_2O_3 catalyst can be reduced to differing extents by various rich or even slightly lean treatments, but is easily re-oxidized at temperatures above 250–300 °C with O_2 . Pt helps maintain Pd in a reduced state, as evidenced by XANES and TPR, which appears to be a major reason for the improved performance of the PtPd catalyst compared to a Pd-only catalyst for the oxidation of hydrocarbons in excess O_2 .

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.05.049>.

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